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Forms and Oscillations Modes of Ion Cloud in the Linear RF-only Quadrupole Traps and in Ion Traps

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Abstract. Computer modelling of space configurations of ion clouds consisting of different m/z ions and dynamics of their motion in the presence of external(dipolar and quadrupolar) RF-field were analysed. Forms of ion clouds in ion traps were obtained by molecular modelling. It was shown that stratification of different m/z ions appears as a result of interaction of ion clouds with RF fields and with each other. For ions with high charge $q=30\ e_{\text{electron}}$ and mass $m=30\ 000\ m_{\text{proton}}$ (electrosprayed protein ions in ion guides and ion traps) at ion densities $\sim 10^8\ \text{cm}^{-3}$ stratification takes place even at room temperatures. Coalescence of ion resonance frequencies for light and heavy equally charged ions in Paul ion trap was also demonstrated.

INTRODUCTION

Different types of ion electromagnetic traps (such as Paul ion trap, linear quadrupole radio-frequency trap, electrodynamic balance etc.) and quadrupole and multipole ion guides are currently in use in different modern mass spectrometers designed for analyses of molecular mixtures at high throughput conditions (proteomics) when ion densities and total ion numbers in traps and guides are high ($>10^6$) and ion-ion interaction is essential to properties of these devices even at room temperatures. In case of linear quadrupole it was found [1,2] that at high ion current in the mode of operation when ions are flying trough a quadrupole and at high charge density in the accumulation mode (ions are accumulated in the quadrupole) large discrimination of ions with different mass to charge ratios (m/z) takes place. Besides, attempts of selective ejection by dipolar excitation of ions of particular m/z in the presence of high space charge revealed collective interaction of ion clouds of different m/z. Attempts were made to explain some aspects of this complex behaviour of such a system in two-dimensional zero temperature approximation [3,4]. The segregation of ions of different m/z occurs similar to segregation of immiscible liquids. Ions of smaller m/z are concentrated closer to the centre of the trap. In case, when supplementary external RF field (dipolar or quadrupolar) is applied to ion ensembles, a complex relative motion of ions with different m/z, interacting through Coulomb forces, takes place. In present work, we approximate an ion cloud by finite number of charges. Each charge interacts as a whole with a field of the trap, and also interacts through Coulomb forces with other charges. The interaction of an ionic cloud with residual gas is described as a

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friction. The ordinary differential equations of ion motion are solved by Euler and fourth order Runge-Kutta methods.

MODEL

Two devices were modelled: Paul ion trap and linear quadrupole trap. An infinitely long wire quadrupole with an infinitely small wire diameter was used as a model for linear quadrupole trap analysis. To trap ions inside such a quadrupole we used two point charges of the same sign as trapped ions positioned on quadrupole axis at some distance from each other. This makes electric field tree dimensional without axial and azimuthal symmetry. Analytical solution for the quadrupolar-dipolar field combination for this electrode geometry significantly simplifies digital analyses of ion behaviour. We suppose that characteristic ion cloud dimension is essentially less than the distance between electrodes. We used a quasi-potential approximation for description of electromagnetic forces in both traps. The value of quasi-potential (Kapitza-Dehmelt effective potential energy [5]) is proportional to the square of radial (and in case of Paul trap to both radial and z-displacement) ion displacement.

3-DIMENSIONAL STATIC CONFIGURATIONS

In the frame of this model we determined the forms of ion clouds for the mixture of different m/z ions at zero temperature. Force acting on i-th charge consists of the electric field force from all ion cloud charges q_k, each of which is positioned at the distance $R_{i,k}$ from charge i

$$E_{i,k} = \Sigma_k q_k \; R_{i,k} \; / |R_{i,k}|^3,$$

the force of the field from two end charges Q

$$E_{END} = \Sigma Q \, (R_i - z) / |R_i - z|^3$$

(here $z = \pm L$ are co-ordinates of end charges) and radial gradient of quasi-potential

$$U = - k \, (x^2 + y^2)/2.$$

Randomly chosen initial ion positions and velocities are relaxing to equilibrium positions. Effective friction of ions in a buffer gas was chosen so that relaxation time was some tens of a charge motion periods in quasi-potential well. We have found different ion cloud configurations with characteristic forms: disc, flattened ellipsoid, spherical ball, elongated ellipsoid, and thread.This sequence of configurations corresponds to growth of the ratio of transversal quasi-potential value to longitudinal one. The length X of linear chain of charged particles as function of ratio of particle charge q to trapping charge Q (placed at points $-L$, $+L$) can be represented approximately by the formula

$$4(Q/q)^{1/2} = (1-x^2)/x^{3/2},$$

$2X=2\,x\,L$ is equilibrium distance between two charges q placed on one line with trapping charges Q. The result of calculations coincides qualitatively with result of experiments [6,11].

STRATIFICATION IN AN ION TRAP

For both linear quadrupole and Paul traps pronounced radial stratification was demonstrated with lower m/z ions dominated near quadrupole axis and the trap centre, similar to what was observed experimentally in Penning trap [7,12] and in linear Paul trap [11]. For linear qudrupole separation of ions according to their m/z was also found in z-direction (along quadrupole axis). The stratification is the result of the balance of the Kapitza-Dehmelt effective potential force from the RF-field and the Coulomb force from the space charge. The dimensionless motion equations for n charges have a form

$$dz/dt = v_z\,,$$
$$dv_z/dt = -z + \Sigma z/r^3\,, \qquad (1)$$

(where summation is taken over all charges in trap) and analogous equations for x,y co-ordinates.

For Paul ion trap the units of time t_l, length t_l and velocity v_l are:

$$t_l = 2 - M z_0^2 \Omega/(Vq),$$

$$z_l = 2M z_0^4 \Omega^2/V^2,$$

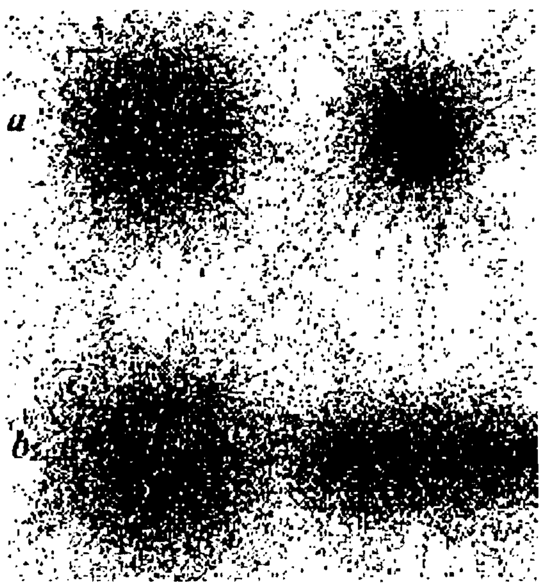

Fig.1. Ion cloud structure as averaged over dimensionless time interval from $t=0$ to $t=10000$.
The beginning of separation at kinetic energy of ions corresponding to $<v_z^2>_{average}=3$ (kinetic energy 300K). Clouds of higher and lower m/z are depicted separately with left cloud corresponding to high m/z and right to lower m/z. *a*- transverse view, *b*- longitudinal view.

Fig.2. Ion cloud structure as averaged over dimensionless time interval from $t=0$ to $t=10000$.
Almost full separation at kinetic energy of ions corresponding to $<v_z^2>_{average}<1$ (kinetic energy <100K). Clouds of higher and lower m/z are depicted separately with left cloud corresponding to high m/z and right to lower m/z. *a*- transverse view, *b*- longitudinal view.

$v_1 = z_1/t_1$., where M is ion mass, z_0 is the half of a distance between end cup electrodes in the ion trap, Ω is a frequency and V an amplitude of RF field. The average kinetic energy of ion longitudinal motion is $M v_1^2/2 <v_z{}^2>_{\text{average}}$. Visual inspection on computer monitor of ion cloud structures obtained as a result of equations (1) solution clearly shows separation of charges with different m/z at $<v_z^2>_{\text{average}} \leq 3$ (Fig.1). Then for $\Omega = 2\pi\ 0.5\ 10^6$ Hz, $M = 3\ 10^4\ Da$, $q = 30$ *elementary charges*, $z_0 = 1\ cm$, $V = 300\ V$, we have $t_1 = 1.4 10^5 s$, $z_1 = 10^{-2}\ cm$, $v_1 = 0.7\ 10^3\ cm/s$ and kinetic energy is $M v_1^2/2 <v_z^2>_{\text{average}} \approx 300\,°K$.

For plasma density $\sim 10^8\ \text{cm}^{-3}$ the kinetic energy is of the order of averaged electrostatic energy per ion q^2/r (r is average distance between ions), so plasma coupling parameter $\Gamma = q^2/(rT) \approx 1$. The same criterion can be find in quite different way. There is a gap between inner droplet and outer envelope in the case of two component (two different m/z ions) system. These ensembles of ions could be considered as charged liquids [12]. The size of the gap has the order of magnitude of the inner droplet radius R. If amplitude of thermally excited surface waves of the droplet

$$x = (T/4\pi\sigma)^{1/2} N^{1/2}$$

($N \approx n^{2/3} R^2$ is full number of surface oscillations) is less than the gap between clouds, $x < R$, then the liquids would be separated, in the opposite case they will be mixed.
We can suppose that

$$\sigma \approx n\, q^2,$$

$q = z^* e$, e is electron charge.

Then liquids would be separated, if

$$n\, q^2\, R^2 > T\, N.$$

So the condition is nearly the same as

$$\Gamma = q^2/(4\pi\, a\, T) > 1,$$

Where $a = (3/(4\pi\ n))^{1/3}$ is Wigner-Seitz interparticle distance. It is possible that the separation can take place even at room temperatures, $n = 10^8\ 1/cm^3$, $z = \sim 30$ as was described in [2]

COLLECTIVE OSCILLATIONS IN ION TRAP

Charged ion cloud oscillations - both longitudinal (z-oscillations) in ion traps [8-9] and transversal in a linear quadrupole traps [1-4] were investigated experimentally. The amplitude of the oscillations (parametric or forced) may be large - of the order of the trap dimensions. Peculiar feature of oscillations is that some characteristic ion frequencies, seen at small ion densities, disappear at higher ones. To model resonance dipolar excitation of ion motion in a Paul trap we applied excitation voltage to end caps of RF-only Paul trap. We have found a strong influence of the space charge value on the ion selection process. Computer modelling revealed strong correlation of ion motion of different m/z, which explains a coalescence of ion resonance peaks, observed experimentally [9] for isotopes of rare earth ions. We studied the coalescence of ion resonance frequencies for 3-D motion of 3 light and 9 heavy (m_2/m_1=1.1) equally charged ions in Paul ion trap. The light and heavy ion clouds are completely separated after relaxation period. The configuration is flat because longitudinal field in Paul trap is twice as large as the radial field. After relaxation an external periodical longitudinal force was applied and friction force was switched off. At small electrostatic ion interaction two resonances were observed with frequencies difference about 10%. As electrostatic interaction increased, this difference goes to zero.

CONCLUSION

Molecular modelling of multicomponent system of charged particles in a RF-traps have shown the possibility of different m/z ion cloud separation even at room temperature in case of multiply charged ions and high plasma densities. Criterion of separation obtained from the analyses of thermally excited surface waves of ion clouds coincides with Γ=1 criterion. Resonance peak coalescence correlate with stratification and takes place at nearly same Γ values.

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